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A Novel Chiral (salen)Al^{III} Complex Catalyzed Asymmetric Cyanosilylation of Aldehydes

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Keywords: Aluminum / Asymmetric synthesis / Cyanides / Enantioselectivity / Aldehydes

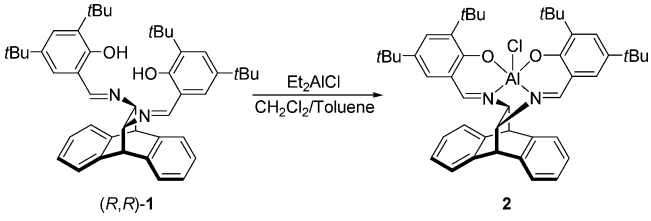
A novel chiral (salen)Al^{III} complex was synthesized through the reaction of Et_2AlCl and salen (*R*,*R*)-**1** derived from (*R*,*R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene. This complex is an efficient catalyst for the asymmetric trimethylsilylcyanation of aldehydes in the presence of tributylphosphane oxide as an additive. The use of 1 mol-% of the complex led to the corresponding cyanohydrins in high yields (85–94 %) with good-to-excellent enantioselectivities (42–92 % *ee*).

Introduction

Optically active cyanohydrins are important intermediates in organic synthesis for the synthesis of a variety of valuable classes of chiral compounds, such as α-amino acids, α-hydroxy carboxylic acids, β-amino alcohols, vicinal diols, and α-hydroxy ketones. Many efficient approaches have been reported for their preparation by biochemical and chemical methods.[1] In the latter, the most important one is the asymmetric silylcyanation of aldehydes with trimethylsilyl cyanide catalyzed by a Lewis acid center, such as Ti^{IV}, Al^{III}, V^{V}, and some lanthanide in the presence of a chiral ligand. Among them, the most widely used and efficient catalysts are chiral Ti^{IV} and chiral Al^{III} complexes.[1b] Significant progress (up to 92–99 % *ee*) was achieved in the Ti^{IV} complex catalyzed asymmetric silylcyanation reaction in the presence of a wide range of chiral ligands, such as the sulfonamide ligands of Choi,[2] salen ligands developed by Belokon, North,[3] and Che,[4] chiral diamide ligands of Uang,[5] and the bifunctional phosphonamide ligand reported by Buono[6] and Tang,[7] respectively. As for the aluminum catalyst, high enantioselectivities (up to >98 % *ee*) were obtained in the presence of the bifunctional 3,3′-disubstituted binol ligand reported by Shibasaki,[8] Najera,[9] and Pu,[10] respectively. Kim reported that the salen ligand derived from cyclohexane-1,2-diamine is an alternative choice. However, the corresponding cyanohydrins were obtained only with a highest selectivity of 86 % *ee*.[11] This was the only example of a (salen)Al^{III} complex catalyzed asymmetric silylcyanation reaction. Recently, we developed novel salen ligand (*R*,*R*)-**1** based on (*R*,*R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene, and we found that the chiral titanium complex formed in situ upon treatment of Ti(O*i*Pr)$_4$ with (*R*,*R*)-**1** was an efficient catalyst for the asymmetric silylcyantion of aldehydes (up to 76 % *ee*).[12] Herein, we report the application of this novel ligand in the aluminum-catalyzed asymmetric silylcyantion of aldehydes.

Results and Discussion

The reaction of (*R*,*R*)-**1** and Et_2AlCl (0.9 M solution in toluene) at room temperature under a nitrogen atmosphere afforded the corresponding (salen)Al^{III} complex **2** as a yellow solid (Scheme 1). With this novel catalyst in hand, the influence of solvent, reaction temperature, additive, and catalyst loading on the reaction were systematically investigated by using the reaction of benzaldehyde and trimethylsilyl cyanide as a model. The results are listed in Table 1.



Scheme 1. Preparation of (salen)Al^{III} complex **2**.

Solvent evaluation revealed that dichloromethane was the best solvent for this reaction in terms of yield and enantioselectivity (Table 1, Entry 1–6). By comparison of the parallel reactions carried out at different temperatures (0, 10, 20 °C), it was found that 10 °C was the optimal reaction temperature for the reaction, which gave the highest enantiocontrol (Table 1, Entry 6; 81 % *ee*). Either lowering or raising the temperature resulted in a little decrease in the

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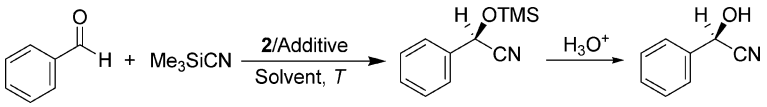
Table 1. Optimization of reaction conditions.

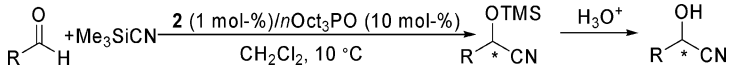


Entry	**2** [mol-%]	Additive (mol-%)	Solvent	*T* [°C]	Time [h]	Yield [%][a]	*ee* [%][b]
1	1	Ph_3PO (10)	acetone	10	18	48	49
2	1	Ph_3PO (10)	THF	10	16	73	68
3	1	Ph_3PO (10)	ethyl acetate	10	16	83	49
4	1	Ph_3PO (10)	$CHCl_3$	10	16	89	73
5	1	Ph_3PO (10)	toluene	10	16	86	60
6	1	Ph_3PO (10)	CH_2Cl_2	10	16	89	81
7	1	Ph_3PO (10)	CH_2Cl_2	0	20	81	75
8	1	Ph_3PO (10)	CH_2Cl_2	20	12	94	80
9	0.5	Ph_3PO (10)	CH_2Cl_2	10	14	94	67
10	2	Ph_3PO (10)	CH_2Cl_2	10	11	94	75
11	1	Ph_3PO (5)	CH_2Cl_2	10	16	92	58
12	1	Ph_3PO (20)	CH_2Cl_2	10	16	93	76
13	1	–	CH_2Cl_2	10	16	90	0
14	1	nBu_3PO (10)	CH_2Cl_2	10	16	93	64
15	1	$nOct_3PO$ (10)	CH_2Cl_2	10	16	93	86

[a] Yield of the isolated product after chromatography on silica gel. [b] Determined by GC analysis of the acetate of the cyanohydrin on a β-DEX120 column, t_{R1} = 23.47 (major) and t_{R2} = 22.35 min (minor).

enantiomeric excess values (Table 1, Entries 7, 8; 75, 80%*ee*, respectively). It was found that the catalyst loading was an essential factor to the reaction. The use of 1 mol-% of catalyst resulted in the best results (Table 1, Entry 6; 81%*ee*), and the *ee* value obviously decreased with adjusting the loading of the catalyst to 0.5 mol-% (Table 1, Entry 9; 67%*ee*) and 2 mol-% (Table 1, Entry 10; 75%*ee*). Moreover, the presence of additive had an important influence on the stereoselectivity of the reaction. For example, mandelonitrile was obtained with 81%*ee* (Table 1, Entry 6) with the introduction of triphenylphosphane oxide as an additive. Although the reaction also ran smoothly in the absence of Ph_3PO, the enantioselectivity was dramatically decreased and racemic mandelonitrile was obtained (Table 1, Entry 13). Kim discovered that Ph_3PO was the best additive when cyclohexane-1,2-damine-derived (salen)-Al complex was employed as the catalyst. So, the influence of additive amount on the reaction was investigated by using Ph_3PO as the additive. The additive quantity was proven to be another key factor to the reaction. For example, the best result was observed in the presence of 10 mol-% of additive (Table 1, Entry 6; 81%*ee*), whereas a decrease or an increase in the amount of Ph_3PO led to a detrimental effect on the stereocontrol (Table 1, Entries 11, 12; 58, 76%*ee*, respectively). Further investigation revealed that the structure of the additive also played an important role on the reaction. Relative to the phosphane oxide containing a short alkyl chain (Table 1, Entry 14; nBu_3PO, 64%*ee*) and triarylphosphane oxide (Table 1, Entry 6: Ph_3PO, 81%*ee*), trioctylphosphane oxide containing a longer alkyl chain demonstrated better enantioselectivity (Table 1, Entry 15; 86%*ee*).

Table 2. (salen)Al^{III} complex **2** catalyzed asymmetric trimethylsilylcyanation of aldehydes.



Entry	R group	Time [h]	Yield [%][a]	$[a]_D^{20}$[b]	*ee* [%][c]	Configuration[d]
1	C_6H_5	16	93	+45.0 (1.06)	86	*S*
2	4-ClC_6H_4	14	86	–28.5 (1.10)	70	*S*
3	2-$MeOC_6H_4$	12	89	+23.7 (1.13)	86	*R*
4	4-$MeOC_6H_4$	12	90	–38.3 (1.04)	81	*S*
5	2-MeC_6H_4	12	94	–33.1 (1.10)	80	*S*
6	3-MeC_6H_4	12	92	–46.2 (1.17)	88	*S*
7	4-MeC_6H_4	12	90	–47.9 (1.02)	92	*S*
8	1-naphthyl	12	85	–49.8 (1.00)	76	*S*
9	2-fury	12	90	–36.1 (1.07)	83	*R*
10	(*E*)-cinnamyl	12	89	–20.9 (1.03)	78	*S*
11	$PhCH_2CH_2$	12	89	–4.8 (1.07)	42	*R*

[a] Yield of the isolated product after chromatography on silica gel. [b] Value in parentheses is the concentration of the sample in $CHCl_3$. [c] Determined by GC analysis of the acetate of the cyanohydrin on a β-DEX120 column. [d] Absolute configuration was assigned by comparison of the sign of specific rotation value with literature.[13–15]

Under the optimal reaction conditions (1 mol-% **2**, 10 mol-% nOct$_3$PO, at 10 °C in CH_2Cl_2), a variety of aldehydes were evaluated, and the results are summarized in Table 2.

As shown in Table 2, chiral (salen)Al^{III} complex **2** demonstrated high efficacy in the transformation of aldehydes into cyanohydrins. In all cases, the corresponding products were obtained in good-to-excellent chemical yields (85–94%) with up to 92%*ee*. Benzaldehydes with various electron-donating substituents and electron-rich heteroaromatic aldehydes, such as 2-furaldehde, were transformed into chiral cyanohydrins in good enantioselectivities (80–92%*ee*). The best result (Table 2, Entry 7; 92%*ee*) was observed for *para*-methyl-substituted benzaldehyde. On the other hand, the introduction of an electron-withdrawing group on the benzene ring disfavored the stereocontrol of the reaction (Table 2, Entry 2; 70%*ee*). 1-Naphthaldehyde gave a slightly lower *ee* value (Table 2, Entry 8; 76% *ee*) than benzaldehyde. Aliphatic aldehydes, such as 3-phenylpropanal and (*E*)-cinnamaldehyde, also reacted smoothly with Me_3SiCN. Moreover, the *ee* value of unsaturated cinnamaldehyde (Table 2, Entry 10; 78%*ee*) was much higher than that of saturated 3-phenylpropanal (Table 2, Entry 11; 42%*ee*).

Conclusions

A highly efficient novel (salen)Al^{III} catalyst based on enantiopure 11,12-diamino-9,10-dihydro-9,10-ethanoanthracene for the asymmetric trimethylsilylcyanation of aldehydes was developed. Under mild conditions, excellent reactivity and enantioselectivity could be generated (up to 94% yield and up to 92%*ee*) with only 1 mol-% of catalyst. Mechanistic studies and further application of this novel catalyst in asymmetric silylcyanation of ketones is ongoing in our laboratory.

Experimental Section

General Methods: All reagents and solvents were commercial grade and purified prior to use when necessary. ^{1}H and ^{13}C NMR were acquired with either a Bruker AMX-300 or a Varian 400 MHz instrument. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ = 7.26 ppm and δ = 77.1 ppm ($CDCl_3$) for ^{1}H and ^{13}C, respectively. Specific rotations were measured with a Perkin–Elmer 341MC polarimeter. Enantiomeric excesses were determined with an Agilent 6890 instrument (β-DEX120 column). Elemental analyses were conducted with a Yanaco CHN Corder MT-3 automatic analyzer. Melting points were determined with a T-4 melting point apparatus and are uncorrected.

Chiral salen Ligand (*R*,*R*)-1: A mixture of (*R*,*R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene (3.47 g, 14.68 mmol), 3,5-di-*tert*-butylsalicylaldehyde (6.88 g, 29.36 mmol), and anhydrous sodium sulfate in chloroform (150 mL) was heated at reflux whilst stirring for 24 h. After removal of sodium sulfate through filtration, the filtrate was condensed to dryness under reduced pressure. The residue was then recrystallized from methanol to afford pure salen ligand (*R*,*R*)-**1** as a yellow solid (7.84 g, 80.0%). M.p. 145–147 °C. $[\alpha]_D^{20}$ = –247.8 (c = 1.01, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 18 H, 2 *t*Bu), 1.38 (s, 18 H, 2 *t*Bu), 3.55 (s, 2 H, 2 CH), 4.27 (s, 2 H, 2 CH), 7.01 (s, 1 H$_{arom}$), 7.02 (s, 1 H$_{arom}$), 7.22–7.24 (m, 4 H$_{arom}$), 7.26 (s, 1 H$_{arom}$), 7.33–7.39 (m, 5 H$_{arom}$), 8.31 (s, 2 H, 2 =CH), 12.70 (br. s, 2 H, 2 OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8, 31.9, 35.4, 52.3, 77.5, 124.3, 126.1, 126.6, 126.8, 127.0, 127.5, 137.1, 140.3, 140.6, 141.2, 158.3, 166.1 ppm. $C_{46}H_{56}N_2O_2$ (668.92): calcd. C 82.59, H 8.44, N 4.19; found C 82.78, H 8.71, N 4.40.

Chiral (salen)Al Complex 2: To a stirring solution of (*R*,*R*)-**1** (1.50 g, 2.20 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of diethylaluminum chloride (0.9 M in toluene, 2.40 mL) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for another 3 h (monitored by TLC). After removal of solvent, the yellow crude product was recrystallized from dry hexane (50 mL) to afford the (salen)Al complex as a yellow solid (1.43 g, 89.4%). M.p. >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 18 H, 2 *t*Bu), 1.38 (s, 18 H, 2 *t*Bu), 3.56 (s, 2 H, 2 CH), 4.28 (s, 2 H, 2 CH), 7.01 (s, 2 H$_{arom}$), 7.22–7.24 (m, 4 H$_{arom}$), 7.33–7.37 (m, 8 H$_{arom}$), 8.31 (s, 2 H, 2 =CH) ppm.

General Procedure for 2-Catalyzed Asymmetric Silylcyanation of Aldehydes: A mixture of (salen)Al complex (7.3 mg, 0.01 mmol), trioctylphosphane oxide (38.7 mg, 0.1 mmol), and dry dichloromethane (3 mL) was stirred for 0.5 h at room temperature under a nitrogen atmosphere. To the mixture was added aldehyde (1 mmol) at 10 °C, and the resulting mixture was stirred for another 0.5 h at the same temperature. Trimethylsilyl cyanide (200 mg, 2 mmol) was then added with a syringe pump. After stirring for 12–18 h at this temperature, the mixture was poured into a mixture of HCl (1 N, 15 mL) and ethyl acetate (30 mL) and stirred for 4 h at room temperature. The organic layer was washed with distilled water and saturated $NaHCO_3$ (each 10 mL) and dried with anhydrous sodium sulfate. The solution was concentrated and purified by column chromatography (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to yield the expected cyanohydrin. The pure cyanohydrin was converted directly into the corresponding acetates by treatment with acetic acid anhydride (2 equiv.) and pyridine (2 equiv.) in CH_2Cl_2 (20 mL) at room temperature for 12 h. The separated organic layer was washed with 5% H_2SO_4, distilled water, and saturated $NaHCO_3$ (each 10 mL), then dried with anhydrous sodium sulfate, and concentrated. The crude acetate was purified by column chromatography (200–300 mesh; petroleum ether/ethyl acetate, 5:1) to provide the acetylated cyanohydrin, which was used for further chiral GC analysis.

(*S*)-(–)-Mandelonitrile (3a): Colorless oil. Yield: 121 mg, 93%. $[\alpha]_D^{20}$ = –45.0 (c = 1.06, $CHCl_3$), 86%*ee*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (br. s, 1 H, OH), 5.53 (s, 1 H, CH), 7.43–7.45 (m, 3 H$_{arom}$), 7.51–7.53 (m, 2 H$_{arom}$) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 23.47 (major), 22.35 (minor) min.

(*S*)-(–)-α-Hydroxy-4-chlorophenylacetonitrile (3b): Colorless oil. Yield: 144 mg, 93%. $[\alpha]_D^{20}$ = –28.5 (c = 1.10, $CHCl_3$), 70%*ee*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28 (br. s, 1 H, OH), 5.52 (s, 1 H, OH), 7.43 (d, J = 8.8 Hz, 2 H$_{arom}$), 7.47 (s, J = 8.8 Hz, 2 H$_{arom}$) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 66.28 (major), 63.46 (minor) min.

(*R*)-(+)-α-Hydroxy-2-methoxyphenylacetonitrile (3c): Colorless oil. Yield: 145 mg, 89%. $[\alpha]_D^{20}$ = +23.7 (c = 1.13, $CHCl_3$), 86%*ee*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (d, J = 9.0 Hz, 1 H, OH), 3.96 (s, 3 H, CH_3), 5.56 (d, J = 9.0 Hz, 1 H, CH), 7.00–7.05 (m, 2 H$_{arom}$), 7.38–7.44 (m, 2 H$_{arom}$) ppm. GC (corresponding acetate, β-DEX120 column); t_R = 67.78 (major), 68.07 (minor) min.

(*S*)-(–)-α-Hydroxy-4-methoxyphenylacetonitrile (3d): Colorless oil. Yield: 147 mg, 90%. $[\alpha]_D^{20}$ = –38.3 (*c* = 1.04, $CHCl_3$), 81%*ee*. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.78 (br. s, 1 H, OH), 3.84 (s, 3 H, CH_3), 5.49 (s, 1 H, CH), 6.96–7.46 (m, 4 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 75.30 (major), 72.97 (minor) min.

(*S*)-(–)-α-Hydroxy-2-methylphenylacetonitrile (3e): Colorless oil. Yield: 138 mg, 94%. $[\alpha]_D^{20}$ = –33.1 (*c* = 1.10, $CHCl_3$), 80%*ee*. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (br. s, 3 H, CH_3), 5.68 (s, 1 H, CH), 7.26–7.43 (m, 4 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 51.16 (major). 50.27 (minor) min.

(*S*)-(–)-α-Hydroxy-3-methylphenylacetonitrile (3f): Colorless oil. Yield: 135 mg, 92%. $[\alpha]_D^{20}$ = –46.2 (*c* = 1.17, $CHCl_3$), 88%*ee*. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 3.30 (br. s, 1 H, OH), 5.47 (s, 1 H, CH), 7.23–7.33 (m, 4 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 53.70 (major), 51.30 (minor) min.

(*S*)-(–)-α-Hydroxy-4-methylphenylacetonitrile (3g): Colorless oil. Yield: 132 mg, 90%. $[\alpha]_D^{20}$ = –47.9 (*c* = 1.02, $CHCl_3$), 92%*ee*. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, CH_3), 3.10 (br. s, 1 H, OH), 5.50 (s, 1 H, CH), 7.25–7.42 (m, 4 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 56.64 (major), 53.58 (minor) min.

(*S*)-(–)-2-Hydroy-2-(1-naphthyl)acetonitrile (3h): Colorless oil. Yield: 156 mg, 85%. $[\alpha]_D^{20}$ = –49.8 (*c* = 1.00, $CHCl_3$), 76%*ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.43 (d, *J* = 6.9 Hz, 1 H, OH), 6.17 (d, *J* = 6.9 Hz, 1 H, CH), 7.42–8.22 (m, 7 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 155.49 (major), 151.58 (minor) min.

(*R*)-(–)-2-(Furan-2-yl)-2-hydroxyacetonitrile (3i): Colorless oil. Yield: 111 mg, 90%. $[\alpha]_D^{20}$ = –36.1 (*c* = 1.07, $CHCl_3$), 83%*ee*. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.31 (br. s, 1 H, OH), 5.57 (s, 1 H, CH), 7.27–7.71 (m, 3 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 26.13 (major), 28.53 (minor) min.

(*S*)-(–)-(*E*)-2-Hydroxy-4-phenylbut-3-enenitrile (3j): Colorless oil. Yield: 142 mg, 89%. $[\alpha]_D^{20}$ = –20.9 (*c* = 1.03, $CHCl_3$), 78%*ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.82 (br. s, 1 H, OH), 5.17 (d, *J* = 4.8 Hz, 1 H, CH), 6.24–6.29 (dd, *J* = 6.0, 15.6 Hz, 1 H, PhC=CH), 6.92 (d, *J* = 15.6 Hz, 1 H, PhHC=C), 7.31–7.38 (m, 3 H_{arom}), 7.41–7.43 (m, 2 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 77.19 (major), 75.36 (minor) min.

(*R*)-(–)-2-Hydroxy-4-phenylbutanenitrile (3k): Colorless oil. Yield: 143 mg, 89%. $[\alpha]_D^{20}$ = –4.8 (*c* = 1.07, $CHCl_3$), 42%*ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.15–2.21 (m, 2 H, CH_2), 2.61 (br. s, 1 H, OH), 2.83–2.88 (m, 2 H, CH_2), 4.43 (t, *J* = 6.9 Hz, 1 H, CH), 7.21–7.24 (m, 3 H_{arom}), 7.30–7.34 (m, 2 H_{arom}) ppm. GC (corresponding acetate, β-DEX120 column): t_R = 67.38 (major), 65.59 (minor) min.

Supporting Information (see footnote on the first page of this article): NMR spectra of the ligand and catalyst, GC spectra of the prepared cyanohydrin acetates.

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